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PATENT SPECIFICATION



NO DRAWINGS

Date of Application and filing Complete
Specification: June 17, 1960.

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No. 21470/60.

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International Classification:—C08g.

COMPLETE SPECIFICATION

Process for the Colour Stabilisation of High Molecular Weight Linear
Thermoplastic Polycarbonates

ERRATUM

SPECIFICATION NO. 893,396

Page 2, line 13, for "phosphate" read "phosphite".

THE PATENT OFFICE,
8th June, 1962

DS 64922/1(6)/R.109 200 5/62 PL

SPECIFICATION NO. 893,396

The inventors of this invention in the sense of being the actual devisers thereof within the meaning of Section 16 of the Patents Act 1949 are Ludwig Bottenbruch, 18 Bodelschwinghstrasse, Krefeld-Bockum, Germany, Gerhard Fritz, of 12 Bodelschwinghstrasse, Krefeld-Bockum, Germany and Hermann Schnell of 39 Am Oberfeld, Krefeld-Uerdingen, Germany. All German citizens.

THE PATENT OFFICE,
28th May, 1962

DS 64327/1(9)/R.109 200 5/62 PL

35 or before or during their working-up.

It is certainly known to add esters of phosphorous acid to certain highly polymeric materials as anti-oxidants or colour stabilisers such as in the case of synthetic rubber (U.S. 40 Specification No. 2,733,226) or in the case of polyethylene terephthalates (U.S. Specification No. 2,650,213; Belgian Specification No. 544,588). However, it was not to be foreseen that these phosphites would have such a strong 45 colour stabilising or colour reducing effect in

agents: diphenyl-hydroxyethyl-cresyl phosphite 80 (b.p. 185—190°C./0.1 mm.Hg.), monophenyl-dihydroxyethyl cresyl phosphite (b.p. 225—235°C./0.1 mm.Hg.) and trihydroxyethyl cresyl phosphate (highly viscous, colourless oil, ²⁰n_D 1.5553. 85

These compounds, in so far as they have not already been described, are easy to produce by known processes; the tri-aryl phosphites, for example, by heating the appropriate phenol

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COMPLETE SPECIFICATION

Process for the Colour Stabilisation of High Molecular Weight Linear Thermoplastic Polycarbonates

We, FARBENFABRIKEN BAYER AKTIENGESELLSCHAFT, a body corporate organised under the laws of Germany, of (22c) Leverkusen Bayerwerk, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:—

The present invention is concerned with a process for the colour stabilisation of high molecular weight linear thermoplastic polycarbonates.

High molecular weight linear thermoplastic polycarbonates which are produced by the reaction of dihydroxy-diaryl-alkanes, -sulphones, -sulphoxides, sulphides or -ethers, or other aromatic dihydroxy compounds or of mixtures of these compounds or of mixtures of the above-mentioned dihydroxy compounds with aliphatic, cycloaliphatic or araliphatic dihydroxy compounds with phosgene or diesters of carbonic acid, show, in some cases, in the case of thermoplastic working-up a more or less strong colouration whereby the objects produced from such polycarbonates receive a yellowish to brownish appearance. Similar colourations can also occur in the case of heating of formed bodies from polycarbonates at elevated temperatures in air.

We have now found that these colourations may be substantially prevented and those which have already occurred cleared up if esters of phosphorous acid are added to the polycarbonates during or after their production or before or during their working-up.

It is certainly known to add esters of phosphorous acid to certain highly polymeric materials as anti-oxidants or colour stabilisers such as in the case of synthetic rubber (U.S. Specification No. 2,733,226) or in the case of polyethylene terephthalates (U.S. Specification No. 2,650,213; Belgian Specification No. 544,588). However, it was not to be foreseen that these phosphites would have such a strong colour stabilising or colour reducing effect in

the case of condensation polymers produced from easily oxidisable phenols and particularly also that they would even be able to lighten products which are already coloured.

There may be used trialkyl, triaryl or mixed aliphatic and aromatic esters, such as tributyl phosphite, trioctyl phosphite, triphenyl phosphite, tri-2-methyl phenyl phosphite, tri-4-tertiary-butyl phenyl phosphite, tri-2-tertiary-butyl phenyl phosphite, tri-2-cyclohexyl phenyl phosphite, tri-2, 6-dimethyl phenyl phosphite (b.p. 165°C./0.03 mm.Hg.), tri-2, 6-diethyl phenyl phosphite (b.p. 187—189°C./0.12 mm.Hg.), and tri-2-methyl-4-tertiary butyl phenyl phosphite (b.p. 214°C./0.03 mm.Hg.).

Particularly suitable are phosphites from aromatic hydroxy compounds in which the aromatic nuclei are substituted in the 2- and 4-positions, or in the 2- and 5-positions by aliphatic or cycloaliphatic radicals containing 1—6 carbon atoms, such as tri-2-methyl-4-tertiary butyl phenyl phosphite (b.p. 214°C./0.03 mm. Hg.), tri-2-tertiary butyl-4-methyl phenyl phosphite (b.p. 182—183°C./0.08 mm. Hg.) and tri-2-tertiary butyl-5-methyl phenyl phosphite (b.p. 202°C./0.06 mm.Hg.), the last-mentioned type being characterised by a particularly high effectiveness.

Mixed aliphatic and aromatic or pure aliphatic phosphites of the following types may be used with particularly good effect as additives in the case of the production of polycarbonates by the transesterification process since they do not act or only act very slightly as cross-linking agents: diphenyl-hydroxyethyl-cresyl phosphite (b.p. 185—190°C./0.1 mm.Hg.), monophenyl-dihydroxyethyl cresyl phosphite (b.p. 225—235°C./0.1 mm.Hg.) and trihydroxyethyl cresyl phosphate (highly viscous, colourless oil, n_D^{20} 1.5553).

These compounds, in so far as they have not already been described, are easy to produce by known processes; the tri-aryl phosphites, for example, by heating the appropriate phenol

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with phosphorous trichloride, hydrogen chloride being split off, and the aliphatic or mixed aromatic-aliphatic phosphites, for example, advantageously by transesterification of, for example, tri-phenyl or tri-cresyl phosphites with the corresponding alcohol when the alcoholic component boils at a higher temperature than the corresponding phenol. The phosphites are, in most cases, purified by fractional distillation and are obtained as colourless, partially syrupy, partially crystalline compounds.

The amounts of phosphate which can be added to the polycarbonates in order to prevent a colouration advantageously lie between about 0.01 and about 1%, preferably between about 0.05 and about 0.2%. Larger amounts certainly exercise a favourable effect on the colour of the polycarbonates but result in a deterioration of the mechanical properties of the polycarbonates.

The addition of the phosphites can take place in different ways. Since most phosphites have oily or solid properties, they are expediently used in the form of solutions in, for example, benzene, petroleum ether, methylene chloride or chloroform, which are added to the polycarbonate granulate, for example, by spraying. The addition of the phosphite is often possible during the production of the polycarbonate. In the case of the production of the polycarbonates by the transesterification process, mixed aliphatic-aromatic phosphites, particularly those of the type described above, are expediently added because these do not, or only slightly, bring about a cross-linking. Since, in the case of this process, the polycarbonate is frequently spun into bristles, these bristles can also be allowed to run through a solution of the phosphite in a low boiling point solvent, a thin phosphite film remaining on the bristles after evaporation of the solvent. In the case of the production of the polycarbonates by phosgenation of the dihydroxy compounds, more or less viscous solutions are frequently obtained which, after having been washed free of electrolytes, can be admixed with the phosphite or a solution thereof. In this case, a particularly homogenous mixture is obtained. Expediently, one chooses, in particular in the case of this method, phosphites which are characterised by a great resistance to hydrolysis, for example, those which carry in the adjacent position to the hydroxyl group of the corresponding hydroxy compound a large substituent, such as tri-*o*-cyclohexyl phenyl phosphite, tri-2-tertiary butyl phenyl phosphite or tri-2-tertiary butyl-5-methyl phenyl phosphite.

The following Examples are given for the purpose of illustrating the present invention, the parts by weight and the parts by volume being in the relationship of grams to millilitres:

EXAMPLE 1

4540 parts by weight bisphenol A and 35 parts by weight *p*-tertiary-butyl phenol are reacted with 2365 parts by weight phosgene in

the presence of 1500 parts water, 1200 parts by weight methylene chloride and 5150 parts by weight 45% sodium hydroxide solution to give a polycarbonate (relative viscosity 1.35). The highly viscous polycarbonate solution in methylene chloride is washed free of electrolytes in a kneader. One half is immediately freed from solvent and the second mixed, by kneading, with a solution of 2.5 parts by weight tri-*o*-cyclo-hexyl-phenyl phosphite in 50 parts by volume methylene chloride and subsequently freed from solvent. The so-obtained granulates are spun to bristles through a worm and are then chopped up to a granulate. The granulate of the material to which phosphite has not been added has an iodine colour number of 3 whereas the phosphite-containing granulate has an iodine colour number of 2. Both granulates are moulded in an injection moulding machine to give test bodies. The phosphite-free test bodies have a colour number of 4—5 and the phosphite containing bodies have a colour number of 3—4.

EXAMPLE 2.

A highly viscous polycarbonate solution in methylene chloride, obtained according to Example 1, is after washing, divided into two parts, one of which is worked-up to a granulate without the addition of phosphite and the other of which is worked up to a granulate after the addition of 2.5 parts by weight tri-2-tertiary butyl-5-methyl phenyl phosphite in 50 parts by volume methylene chloride. After extrusion, the phosphite-containing granulate yields a granulate with a colour number of 1—2 and the phosphite-free material gives a granulate with a colour number of 3. The test bodies obtained from these granulates by injection moulding show colour numbers of 2 and 4—5, respectively.

EXAMPLE 3.

A phosphite-free granulate (2500 parts by weight) obtained according to Example 1 is sprayed with frequent turning with a solution of 2.0 parts by weight tri-*o*-cyclo-hexyl phenyl phosphite in 50 parts by volume petroleum ether and dried in a drying chamber. The granulate obtained after extrusion has a colour number of 2 and the test bodies produced by injection moulding have a colour number of 3—4.

EXAMPLE 4.

7000 parts by weight bisphenol A are transesterified to give a high molecular polycarbonate under the usual conditions with 6600 parts by weight diphenyl carbonate and 0.1 parts by weight sodium bisphenolate-A as catalyst. The granulate obtained after spinning and chopping up the bristles has a colour number of 3.

When 4.0 parts by weight (0.05%) mono-phenyl-dihydroxy-ethyl-cresyl phosphite are added to the reaction mixture before the transesterification, then a granulate with a colour number of 2 is obtained.

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WHAT WE CLAIM IS:—

1. Process for the colour stabilization of high molecular weight, linear, thermoplastic polycarbonates, wherein a tertiary ester of phosphorous acid is added to the polycarbonate during or after its production or before or during the working up thereof.
2. Process according to claim 1, wherein the ester is added in an amount of between 0.01 and 1%.
3. Process according to claim 2, wherein the ester is added in an amount of between 0.05 and 0.2%.
4. Process according to any of the preceding claims, wherein the ester used contains at least one residue of an aromatic hydroxy compound containing aliphatic or cycloaliphatic radicals with 1 to 6 carbon atoms in the 2- and 4-positions or the 2- and 5-positions of the aromatic nucleus.
5. Process according to any of claims 1 to 3,

wherein the ester used is a mixed aliphatic-aromatic ester or an aliphatic ester.

6. Process according to any of claims 1 to 3, wherein the ester used is any of those hereinbefore specified.

7. Process for the colour stabilization of high molecular weight, linear, thermoplastic polycarbonates, substantially as hereinbefore described and with reference to any of the specific Examples.

8. High molecular weight, linear, thermoplastic polycarbonates, whenever colour stabilized by the process according to any of claims 1—7.

9. High molecular weight, linear, thermoplastic polycarbonates, with a content of a tertiary ester of phosphorous acid.

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